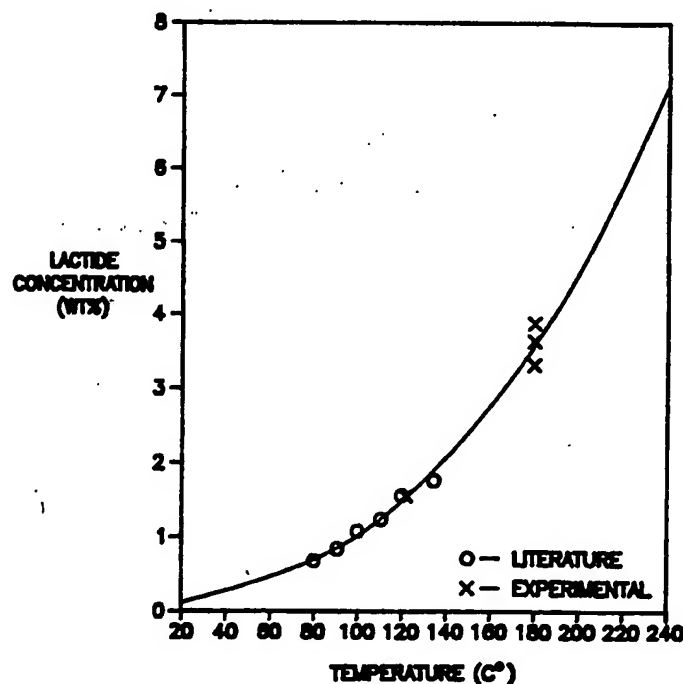




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**(54) Title:** A MELT-STABLE LACTIDE POLYMER FABRIC AND PROCESS FOR MANUFACTURE THEREOF

**(57) Abstract**

A nonwoven fabric comprised of a lactide polymer. The lactide polymer comprises a plurality of poly(lactide) polymer chains, residual lactide in concentration of less than about 2% and water in concentration of less than about 2000 parts-per-million. A process for manufacturing a nonwoven fabric with the lactide polymer composition is also disclosed.

**A MELT-STABLE LACTIDE POLYMER FABRIC  
AND PROCESS FOR MANUFACTURE THEREOF**

**BACKGROUND OF THE INVENTION**

**1. Field of the Invention**

5       The present invention relates to fabrics comprising a melt-stable, biodegradable lactide polymer composition and a process for manufacturing such fabrics from a melt-stable, biodegradable lactide polymer.

**2. Description of the Prior Art**

10       The need for and uses of fabrics, particularly nonwoven fabrics, have increased tremendously in recent years. Production of nonwoven roll goods was estimated at 2.5 billion pounds in 1992. Nonwoven fabrics are presently used for coverstock, interlinings, wipes,  
15 carrier sheets, furniture and bedding construction, filtration, apparel, insulation, oil cleanup products, cable insulating products, hospital drapes and gowns, battery separators, outerwear construction, diapers and feminine hygiene products.

20       There are basically three different manufacturing industries which make fabrics, such as nonwovens; the textile, paper and extrusion industries. The textile industry garnets, cards or aerodynamically forms textile fibers into oriented webs. The paper industry employs  
25 technology for converting dry laid pulp and wet laid paper systems into nonwoven fabrics. The extrusion industry uses at least three methods of nonwoven manufacture, those being the spunbond, melt blown and porous film methods. The melt blown method involves  
30 extruding a thermoplastic resin through a needle thin die, exposing the extruded fiber to a jet of hot air and depositing the "blown" fiber on a conveyor belt. These fibers are randomly orientated to form a web. The spunbond method also utilizes a needle thin die, but  
35 orients or separates the fibers in some manner. The porous film method employs both slit and annular dies. In one method, a sheet is extruded and drawn, fibrillization occurs and a net-like fabric results.

In order to meet projected needs for biodegradable packaging materials, others have endeavored to optimize lactide polymer processing systems. Gruber et al. (U.S. Pat. No. 5,142,023) disclose a continuous process for  
5 the manufacture of lactide polymers with controlled optical purity from lactic acid having physical properties suitable for replacing present petrochemical-based polymers.

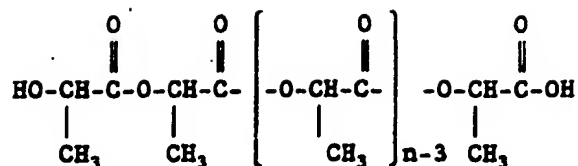
Generally, manufacturers of polymers utilizing  
10 processes such as those disclosed by Gruber et al. will convert raw material monomers into polymer beads, resins or other pelletized or powdered products. The polymer in this form may then be then sold to end users who convert, i.e., extrude, blow-mold, cast films, blow  
15 films, thermoform, injection-mold or fiber-spin the polymer at elevated temperatures to form useful articles. The above processes are collectively referred to as melt-processing. Polymers produced by processes such as those disclosed by Gruber et al., which are to  
20 be sold commercially as beads, resins, powders or other non-finished solid forms are generally referred to collectively as polymer resins.

Prior to the present invention, it is believed that there has been no disclosure of a combination of  
25 composition control and melt stability requirements which will lead to the production of commercially viable lactide polymer nonwoven fabrics.

It is generally known that lactide polymers or poly(lactide) are unstable. The concept of instability  
30 has both negative and positive aspects. A positive aspect is the biodegradation or other forms of degradation which occur when lactide polymers or articles manufactured from lactide polymers are discarded or composted after completing their useful  
35 life. A negative aspect of such instability is the degradation of lactide polymers during processing at elevated temperatures as, for example, during melt-

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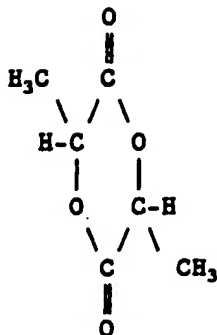
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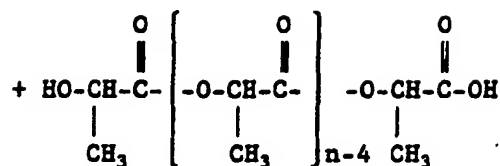
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No consensus has been reached as to what the primary degradation pathways are at elevated processing temperatures. One of the proposed reaction pathways includes the reaction of a hydroxyl end group in a "back-biting" reaction to form lactide. This equilibrium reaction is illustrated above. Other proposed reaction pathways include: reaction of the hydroxyl end group in a "back-biting" reaction to form cyclic oligomers, chain scission through hydrolysis of the ester bonds, an intramolecular beta-elimination reaction producing a new acid end group and an unsaturated carbon-carbon bond, and radical chain decomposition reactions. Regardless of the mechanism or mechanisms involved, the fact that substantial degradation occurs at elevated temperatures, such as those used by melt-processors, creates an obstacle to use of lactide polymers as a replacement for petrochemical-based polymers. It is apparent that degradation of the polymer during melt-processing must be reduced to a commercially acceptable rate while the

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substantial degradation occurs and the molecular weight drops significantly during processing. Also, the polymer may be precipitated from a solvent in order to remove residual monomer and catalysts. Each of these treatments add stability to the polymer, but clearly at a high cost which would not be feasible for lactide polymer compositions which are to be used to replace inexpensive petrochemical-based polymers in the manufacture of nonwoven products.

Furthermore, it is well-known that an increase in molecular weight generally results in an increase in a polymer's viscosity. A viscosity which is too high can prevent melt-processing of the polymer due to physical/mechanical limitations of the melt-processing equipment. Melt-processing of higher molecular weight polymers generally requires the use of increased temperatures to sufficiently reduce viscosity so that processing can proceed. However, there is an upper limit to temperatures used during processing. Increased temperatures increase degradation of the lactide polymer, as the previously-cited studies disclose.

Jamshidi et al., Polymer, Vol. 29, pp. 2229-2234 (1988) disclose that the glass transition temperature of a lactide polymer,  $T_g$ , plateaus at about 57°C for poly(lactide) having a number average molecular weight of greater than 10,000. It is also disclosed that the melting point,  $T_m$ , of poly (L-lactide) levels off at about 184°C for semi-crystalline lactide polymers having a number average molecular weight of about 70,000 or higher. This indicates that at a relatively low molecular weight, at least some physical properties of lactide polymers plateau and remain constant.

Sinclair et al. (U.S. Patent No. 5,180,765) disclose the use of residual monomer, lactic acid or lactic acid oligomers to plasticize poly(lactide) polymers, with plasticizer levels of 2-60%. Loomis (U.S. Patent No.

**SUMMARY OF THE INVENTION**

According to the present invention, a fabric, such as a nonwoven fabric, comprising poly(lactide) fibers is provided. A first portion of the fibers comprises a melt-stable lactide polymer composition comprising: poly(lactide) chains having a number average molecular weight of at least 10,000, and preferably from about 10,000 to about 300,000; lactide in a concentration of less than about 2% by weight; and optionally water in a concentration of less than about 2,000 parts per million. A process for the manufacture of the fabric is also provided. For the purposes of the present invention, the fabric may be manufactured from any number of methods and is not to be limited by the particular method.

Optionally, stabilizing agents in the form of anti-oxidants and water scavengers may be added. Further, plasticizers, nucleating agents and/or anti-blocking agents may be added. The resultant fabric is biodegradable and may be disposed of in an environmentally sound fashion.

Poly(lactide) is a polymeric material which offers unique advantages as a fiber for nonwovens not only in the biodegradable sense, but in the manufacturing process as well.

Poly(lactide) offers advantages in the formation of the nonwoven fabric in a melt extrusion process. One problem that is sometimes encountered in the extrusion of fibers into a nonwoven web is poor adhesion of the fibers to one another upon cooling. Two characteristics of poly(lactides) lend themselves to enhanced adhesion: low viscosity and high polarity. Mechanical adhesion, the interlocking of fibers at adjoining points, increases as the viscosity decreases. An advantage of poly(lactide) is that the viscosity lends itself well to fiber formation. Thus, poly(lactide) fibers adhere to one another well, resulting in a web with added

present nonwoven fabric, when used as a leaf bag, decomposes along with the leaves, thus minimizing the adverse environmental impact of the leaf bags.

Poly(lactide) processes at lower temperatures which  
5 allows the fiber to be extruded at lower temperatures than traditional polymers. This results in a cost savings to the converter because the extrusion equipment will not require as much power when run at lower temperatures. There is also increased safety associated  
10 with lower temperatures.

A significant advantage of poly(lactide) over many fabrics used today such as polypropylene is its biodegradability. The continued depletion of landfill space and the problems associated with incineration of  
15 waste have led to the need for development of a truly biodegradable fabric to be utilized as a substitute for non-biodegradable or partially biodegradable petrochemical-based nonwoven fabrics. Furthermore, a poly(lactide) nonwoven web, unlike other biodegradable  
20 polymers, is believed not to support microbial growth. Starch or other biodegradable polymers, when exposed to warm, damp environments, will promote the growth of unhealthy microbes. This is undesirable in the diaper industry. Thus the present invention has yet another  
25 advantage over prior biodegradable polymers.

The above described features and advantages along with various other advantages and features of novelty are pointed out with particularity in the claims of the present application. However, for a better  
30 understanding of the invention, its advantages, and objects attained by its use, reference should be made to the drawings which form a further part of the present application and to the accompanying descriptive matter in which there is illustrated and described preferred  
35 embodiments of the present invention.

Furthermore, lactide polymers are compostable as illustrated in Example 15 below. Applicants believe the hydrolysis of the ester may be the key to or the first step in degradation of a lactide polymer composition.

5 The mechanism of degradation is not key to the fabric of the present invention, however it must be recognized that such degradation makes lactide polymers desirable as replacements for presently-utilized non-degradable petrochemical-based polymers used for fabrics, such as  
10 nonwovens.

Applicants have found that the instability of lactide polymers which leads to the beneficial degradation discussed above also creates processing problems. These processing problems include generation  
15 of lactide monomer at elevated temperatures and loss in molecular weight believed due to chain scission degradation of the ester bonds and other depolymerization reactions which are not completely understood. No consensus has been reached as to what  
20 are the primary degradation pathways at elevated processing temperatures. As previously disclosed, these may include such pathways as equilibrium-driven depolymerization of lactide polymers to form lactide and chain scission through hydrolysis of the ester bonds  
25 along with other pathways. For purposes of the present invention, the exact mechanism of degradation at elevated temperatures is not critical.

It is to be understood, however, that degradation of lactide polymers is both beneficial and detrimental.  
30 Benefits derive from degradability when articles manufactured from such polymers are discarded. The same or similar types of degradation are detrimental if they occur during processing or prior to the end of the article's useful life.



sufficient quantity to foul or coat processing equipment. The melt-stable lactide polymer exhibits reduced degradation and/or reduced lactide formation relative to known lactide polymers. It is to be understood that degradation will occur during melt-processing. The compositional requirements and use of stabilizing agents as disclosed herein reduces the degree of such degradation to a point where physical properties are not significantly affected by melt-processing and fouling by impurities or degradation by-products such as lactide does not occur. Furthermore, the melt-stable polymer should be melt-processable in melt-processing equipment such as that available commercially. Further, the polymer will preferably retain adequate molecular weight and viscosity. The polymer should preferably have sufficiently low viscosity at the temperature of melt-processing so that the extrusion equipment may create an acceptable nonwoven fabric. The temperature at which this viscosity is sufficiently low will preferably also be below a temperature at which substantial degradation occurs.

#### Polymer Composition

The melt-stable lactide polymer fabric of the present invention comprises poly(lactide) polymer chains having a number average molecular weight of at least 10,000 and preferably from about 10,000 to about 300,000. In a preferred composition for a melt blown nonwoven, the number average molecular weight ranges from about 15,000 to about 100,000. In the most preferred composition, the number average molecular weight ranges from about 20,000 to about 80,000. In a spunbond nonwoven fabric, the preferred number average molecular weight range is from about 50,000 to about 250,000. In a most preferred embodiment, the number average molecular weight range is from about 75,000 to about 200,000.

the remainder being substantially all L-lactide.

For applications where an amorphous polymer is desired, the preferred composition of the reaction mixture is above 9% by weight meso-lactide and a more preferred composition contains above 12% by weight meso-lactide with the remaining lactide being substantially all L-lactide mixture, or D-lactide can be used to control the potential crystallinity in a predominantly L-lactide mixture.

10 Addition of even small amounts of meso-lactide to the polymerization mixture results in a polymer which is even slower to crystallize than polymerization mixtures having lesser amounts of meso-lactide, as detailed in Example 23. Beyond about 12% meso content the polymer  
15 remains essentially amorphous following a typical annealing procedure. This contrasts with the behavior of D,L-lactide, which can be added at a concentration of 20% to the polymerization mixture and still produce a semi-crystalline polymer following the annealing  
20 procedure. These results are detailed in Example 24.

There are three main methods to increase the rate of crystallization. One is to increase chain mobility at low temperatures, by adding, for example, a plasticizing agent. The plasticizer must be selected carefully,  
25 however, and preferably will be of limited compatibility so that it will migrate to the amorphous phase during crystallization. Dioctyl adipate is an example of a plasticizer which helps crystallization rates in poly(lactide), as detailed in Example 25. A second  
30 method to increase the rate of crystallization is to add a nucleating agent, as detailed in Example 26. A third method is to orient the polymer molecules. Orientation can be accomplished by drawing during film casting, drawing of fibers, blowing films, stretching of film or  
35 sheet after it is cast (in multiple directions, if desired), or by the flow of polymer through a small opening in a die. The alignment generated helps to

The water concentration within the melt-stable lactide polymer composition is less than about 2,000 parts-per-million. Preferably this concentration is less than 500 parts-per-million and most preferably less than about 100 parts-per-million. As detailed in Example 14, the polymer melt-stability is significantly affected by moisture content. Thus, the melt-stable polymer of the present invention must have the water removed prior to melt-processing. Applicants recognize that water concentration may be reduced prior to processing the polymerized lactide to a resin. Thus, moisture control could be accomplished by packaging such resins in a manner which prevents moisture from contacting the already-dry resin. Alternatively, the moisture content may be reduced at the melt-processor's facility just prior to the melt-processing step in a dryer. Example 14 details the benefit of drying just prior to melt-processing and also details the problems encountered due to water uptake in a polymer resin if not stored in a manner in which moisture exposure is prevented or if not dried prior to melt-processing. As detailed in these examples, Applicants have found that the presence of water causes excessive loss of molecular weight which may affect the physical properties of the melt-processed polymer.

In a preferred composition of the present invention, a stabilizing agent is included in the polymer formulation to reduce degradation of the polymer during production, devolatilization, drying and melt processing by the end user. The stabilizing agents recognized as useful in the present nonwoven fibers may include antioxidants and/or water scavengers. Preferred antioxidants are phosphite-containing compounds, hindered phenolic compounds or other phenolic compounds. The antioxidants include such compounds as trialkyl phosphites, mixed alkyl/aryl phosphites, alkylated aryl phosphites, sterically hindered aryl phosphites,

Selection of a plasticizing agent requires screening of many potential compounds and consideration of several criteria. For use in a biodegradable nonwoven fabric the preferred plasticizer is to be biodegradable, non-  
5 toxic and compatible with the resin and relatively nonvolatile.

Plasticizers in the general classes of alkyl or aliphatic esters, ether, and multi-functional esters and/or ethers are preferred. These include alkyl  
10 phosphate esters, dialkylether diesters, tricarboxylic esters, epoxidized oils and esters, polyesters, polyglycol diesters, alkyl alkylether diesters, aliphatic diesters, alkylether monoesters, citrate esters, dicarboxylic esters, vegetable oils and their  
15 derivatives, and esters of glycerine. Most preferred plasticizers are tricarboxylic esters, citrate esters, esters of glycerine and dicarboxylic esters. Citroflex A4<sup>®</sup> from Morflex is particularly useful. These esters are anticipated to be biodegradable. Plasticizers  
20 containing aromatic functionality or halogens are not preferred because of their possible negative impact on the environment.

For example, appropriate non-toxic character is exhibited by triethyl citrate, acetyltriethyl citrate,  
25 tri-n-butyl citrate, acetyltri-n-butyl citrate, acetyltri-n-hexyl citrate, n-butyltri-n-hexyl citrate and dioctyl adipate. Appropriate compatibility is exhibited by acetyltri-n-butyl citrate and dioctyl adipate. Other compatible plasticizers include any  
30 plasticizers or combination of plasticizers which can be blended with poly(lactide) and are either miscible with poly(lactide) or which form a mechanically stable blend. Corn oil and mineral oil were found to be incompatible when used alone with poly(lactide) because of phase  
35 separation (not mechanically stable) and migration of the plasticizer.

Organic fillers include a variety of forest and agricultural products, either with or without modification. Examples include cellulose, wheat, starch, modified starch, chitin, chitosan, keratin, 5 cellulosic materials derived from agricultural products, gluten, nut shell flour, wood flour, corn cob flour, and guar gum. Preferred organic fillers are derived from renewable sources and are biodegradable. Fillers may be used either alone or as mixtures of two or more fillers. 10 Example 5 highlights useful anti-blocking fillers for the present invention.

Surface treatments may also be used to reduce blocking. Such treatments include corona and flame treatments which reduce the surface contact between the 15 poly(lactide) based fabric and the adjacent surface.

For certain applications, it is desirable for the fabric to be modified to alter the water transport properties. Surfactants may be incorporated into the web of the present invention to increase the water 20 transport properties.

Surfactants which are useful can be subdivided into cationic, anionic, and nonionic agents.

With regard to cationic compounds, the active molecule part generally consists of a voluminous cation 25 which often contains a long alkyl residue (e.g. a quaternary ammonium, phosphonium or sulfonium salt) whereby the quaternary group can also occur in a ring system (e.g. imidazoline). In most cases, the anion is the chloride, methosulfate or nitrate originating from 30 the quaternization process.

In the anionic compounds, the active molecule part in this class of compounds is the anion, mostly an alkyl sulfonate, sulfate or phosphate, a dithiocarbamate or carboxylate. Alkali metals often serve as cations.

35 Nonionic antistatic agents are uncharged surface-active molecules of a significantly lower polarity than the above mentioned ionic compounds and include

preferred composition, the residual catalyst level in the resin is present in a molar ratio of initial monomer-to-catalyst greater than about 3,000:1, preferably greater than about 5,000:1 and most preferably greater than about 10,000:1. Applicants believe a ratio of about 20,000:1 may be used, but polymerization will be slow. Optimization of catalyst levels and the benefits associated therewith are detailed in Example 20. Applicants have found that when the catalyst level is controlled within these parameters, catalytic activity is sufficient to polymerize the lactide while sufficiently low to enable melt-processing without adverse effect when coupled with low residual monomer level and low water concentration as described above in polymers of molecular weight between 10,000 to about 300,000. It is believed in most applications the addition of a stabilizing agent may be unnecessary if catalyst level is optimized.

Applicants have also found that catalyst concentration may be reduced subsequent to polymerization by precipitation from a solvent. Example 21 demonstrates potential catalyst removal by precipitation from a solvent. This produces a resin with reduced catalyst concentration. In an alternative embodiment, the catalyst means for catalyzing the polymerization of lactide to form the poly(lactide) polymer chains which was incorporated into the melt-stable lactide polymer composition during polymerization is deactivated by including in the melt-stable lactide polymer composition a catalyst deactivating agent in amounts sufficient to reduce catalytic depolymerization of the poly(lactide) polymer chains. Example 11 details the benefits of utilizing a catalyst deactivating agent. Such catalyst-deactivating agents include hindered, alkyl, aryl and phenolic hydrazides, amides of aliphatic and aromatic mono- and dicarboxylic acids, cyclic amides, hydrazones and bishydrazones of aliphatic and

99.5% by weight or less L-lactide and/or D-lactide. Such purified lactide stream may be such as that produced in the process disclosed by Gruber et al., although the source of lactide is not critical to the present invention.

The lactide mixture is polymerized to form a lactide polymer or poly(lactide) with some residual unreacted monomer in the presence of a catalyst means for catalyzing the polymerization of lactide to form poly(lactide). Catalysts suitable for such polymerization have been listed previously. The concentration of catalysts utilized may be optimized as detailed in the following examples and discussed previously.

In a preferred embodiment, a stabilizing agent, which may be an antioxidant and/or a water scavenger is added to the lactide polymer. It is recognized that such stabilizing agents may be added simultaneously with or prior to the polymerization of the lactide to form the lactide polymer. The stabilizing agent may also be added subsequent to polymerization.

As previously disclosed, the catalyst usage is adjusted and/or deactivation agent is added in a sufficient amount to reduce depolymerization of poly(lactide) during melt-processing to less than 2% by weight generation of lactide from a devolatilized sample in the first hour at 180°C and atmospheric pressure. More preferably, the stabilizing agent controls lactide generation to less than 1% by weight and most preferably less than 0.5% by weight in the first hour at 180°C and atmospheric pressure. Alternatively, the control of catalyst concentration to optimize the balance between necessary catalytic activity to produce poly(lactide) versus the detrimental effects of catalytic depolymerization or degradation of the lactide polymer may be utilized to obviate the need for adding a stabilizing agent.

scavenger may also be added through the pipeline (2). The stabilized lactide mixture is fed through a pipeline (4) to a polymerization process (5). The polymerized lactide or lactide polymer leaves the polymerization process through a pipeline (6). The stream is fed to a second mixing vessel (8) within which a stabilizing agent and/or catalyst deactivating agent may be added through a pipeline (7). The stabilized lactide polymer composition is then fed to a devolatilization process (10) through a pipeline (9). Volatile components leave the devolatilization process through a pipeline (11) and the devolatilized lactide polymer composition leaves the devolatilization process (10) in a pipeline (12). The devolatilized lactide composition is fed to a resin-finishing process (14). Within the resin-finishing process the polymer is solidified and processed to form a pelletized or granular resin or bead. Applicants recognize the polymer may be solidified and processed to form resin or bead first, followed by devolatilization. The resin is then fed to a drying process (16) by conveyance means (15). Within the drying process (16) moisture is removed as a vapor through pipeline (17). The dried lactide polymer resin leaves the drying process (16) by a conveyance means (18) and is fed to a melt-processing apparatus (19). Within the melt-processing apparatus (19) the resin is converted to a useful article as disclosed above. The useful article leaves the melt-processing apparatus (19) through a conveyance means (20).

The following examples further detail advantages of the system disclosed herein:

#### Example 1

##### Melt Spinning of Poly(lactide)

Melt spinning of poly(lactide) having a weight average molecular weight of 140,000, a residual lactide content of about 1.1% and an original lactide mixture of



apparatus is a series of rolls, including an unwind roll on the front and a take-up roll on the back. With the take up roll rotating faster than the unwind roll, the fiber is stretched. The rolls in between the unwind and take-up are heated to a temperature of 50°C to soften the polymer and allow the fiber to be drawn. Measuring fiber diameter allows calculation of the draw ratio and birefringence relates to the degree of orientation of the polymer chains. Table 2 summarizes the drawing data. The data illustrates it is possible to postdraw the fibers to increase the orientation of the fibers.

15

Table 2

|    | <u>Initial<br/>Diameter</u> | <u>Final<br/>Diameter</u> | <u>Draw<br/>Ratio</u> | <u>Birefringence<br/>x 1000</u> |
|----|-----------------------------|---------------------------|-----------------------|---------------------------------|
| 20 | 45.00                       | 26.00                     | 3.00                  | 16.64                           |
|    | 45.00                       | 25.10                     | 3.18                  | 19.73                           |
|    | 45.00                       | 24.80                     | 3.32                  | 21.94                           |
| 25 | 45.00                       | 24.00                     | 3.50                  | 19.58                           |

Example 2Properties of Poly(lactide) Melt Spun Fibers.

In an apparatus similar to that used in Example 1, poly(lactide) having a weight average molecular weight of about 100,000, a residual lactide content of less than about 1% and an original lactide mixture of about 10% by weight of meso-lactide was melt spun into a fiber. The optical composition was such that upon annealing, (the sample was held at 100°C for 90 minutes, the oven was turned off and was allowed to cool to room temperature), the polymer exhibited an endothermic melt peak with a peak temperature of 140°C with an endotherm of 36.1 joules/gram.

Table 3

| <u>Properties</u>          | <u>Resin</u> | <u>As-Spun</u> | <u>Drawn</u> | <u>Polyprop.</u> | <u>Nylon 6,6</u> |
|----------------------------|--------------|----------------|--------------|------------------|------------------|
| 5 Melt Temp (°C)           | 133          | 140            | 140          | 170              | 265              |
| Heat of Fusion (J/g)       | 2.4          | 14.2           | 26.4         | 105              | xxxxx            |
| Denier (g/9000m)           | xxxxx        | 162            | 57           | xxxxx            | xxxxx            |
| Tenacity (g/den)           | xxxxx        | 0.97           | 2.75         | 6.5              | 5.4              |
| Break Elongation           | xxxxx        | 165%           | 38%          | 34%              | 20%              |
| 10 Young's Modulus (g/den) | xxxxx        | 22             | 44           | 68               | 34               |

particles. The filtration test involved making a 20 gram/liter NaCl solution and making an aerosol of the solution with a concentration of 100 milligram per cubic meter. The aerosol was thereafter passed through the fabric at 31 liters/minute. Sensors were placed both upstream and downstream of the fabric, with the difference reflecting the amount remaining in the filter. Air permeability, another feature important to filtration, was measured according to ASTM D737-75 and reported as cubic feet of air per square feet of fabric per minute. All of these performance measures were compared to standard polypropylene fabrics. The data illustrates poly(lactide) processes as well as polypropylene. Poly(lactide) is capable of forming fine or small diameter fibers. Fibers having diameters of less than about 5  $\mu\text{m}$  are shown. Further, poly(lactide) nonwoven webs have a high filtration efficacy as well as good air permeability. The results are shown in Table 4.

Example 4Melt Blow Nonwovens made from Poly(lactide).

Melt blown fabrics were made with poly(lactide) using the same equipment and procedure as in Example 3. The  
5 extrusion temperature was 320°F, screw speed was 8 rpm, die temperature was 315°F, air temperature and air velocity were at 400°F and 12 cu ft/min/inch web respectively. Die-to-collector distance was 13 inches.

The poly(lactide) used in this test had a weight  
10 average molecular weight of about 66,000, a residual lactide concentration of about 1.3% and an original lactide mixture of about 9% by weight of meso-lactide. This lower molecular weight resulted in softer nonwoven fabrics than Example 3 and had good hand. Fiber diameters were measured  
15 and found to be 11.57  $\mu\text{m}$ . Other tests done on this fabric was the air permeability test having a value of 4.26, bursting strength having a value of 5.4, and filtration efficiency having a value of 14.0%.

Example 520 Anti-Blocking Agents

Two injection molded disks, 2.5 inch diameter, were placed together with a 94 gram weight on top and held at 50°C for 24 hours. The disks had the following agents compounded therein. The disks were then cooled to room  
25 temperature and pulled apart by hand and ranked for blocking characteristics (considerable, slight and none). The following are the results:

Table 6

|    | <u>SAMPLE</u>       | <u>T<sub>g</sub>(C)</u> | <u>Change in T<sub>g</sub>/wt.<br/>percent additive</u> |
|----|---------------------|-------------------------|---|
|    | Control             | 54.8                    | ---   |
| 5  | 8% Dioctyl adipate  | 35.0                    | 2.5   |
|    | Control+40% silica  | 54.5                    | ---   |
|    | Control+40% silica+ |                         |   |
|    | 5% dioctyl adipate  | 36.0                    | 3.7   |
| 10 | Control             | 54.6                    | ---   |
|    | 6% Citroflex A-4*   | 42.6                    | 2.0   |
|    | 12% Citroflex A-4   | 31.4                    | 1.9   |
| 15 | Control             | 59.3                    | ---   |
|    | 1.6% Citroflex A-4  | 56.3                    | 1.9   |
|    | 2.9% Citroflex A-4  | 53.1                    | 2.1   |
|    | Control             | 58.4                    | ---   |
| 20 | 2.1% Citroflex A-4  | 56.1                    | 1.1   |
|    | 3.4% Citroflex A-4  | 50.5                    | 2.3   |
|    | Control             | 61.6                    | ---   |
|    | 18.6% Citroflex A-2 | 54.7                    | 0.4   |
| 25 | 13.1% Citroflex B-6 | 52.4                    | 0.7   |
|    | 12.6% Citroflex A-6 | 53.8                    | 0.6   |

\*Citroflex is a registered trademark of Morflex, Inc.,  
 30 Greensboro, NC. A-4 is the designation of acetyltri-n-butyl citrate. A-2 is the designation of acetyltriethyl citrate, A-6 is the designation of acetyltri-n-hexyl citrate, and B-6 is the designation of n-butyryltri-n-hexyl citrate.

35 These results show the effectiveness of these plasticizers in reducing the glass transition temperature of poly(lactide).

The procedure above was tried using corn oil as a plasticizer. Visual observation showed the corn oil to be  
 40 not compatible, forming a film on the surface. Corn oil and mineral oil were both not effective as a primary plasticizer with poly(lactide). They may still be useful as a secondary plasticizer, in combination with a compatible primary plasticizer.

Example 8Lactide Polymerization in the Presence  
of a Solid Supported Catalyst5      Tin (II) Oxide

24 grams of L-lactide (melting point about 97°C) and 6 grams of D,L-lactide (for the purposes of this invention, D,L-lactide has a melting point of about 126°C) were combined in a round bottom flask with 0.033 grams of Tin (II) oxide, as a fine powder. This corresponds to the catalyst level of 852:1, molar ratio lactide to tin. The flask was then purged with dry nitrogen 5 times. This was lowered into an oil bath at 160°C with magnetic stirring. Polymerization time was 8 hours.

15      Amberlyst 36

24 grams of L-lactide and 6 grams of D,L-lactide were combined in a round bottom flask with 1.06 grams of Amberlyst 36 resin beads. The flask was purged 5 times with dry nitrogen. The flask was lowered into an oil bath at 140°C with magnetic stirring. Polymerization time was 8 hours. The resin had a stated proton content of 1 meq/gram dry weight resin. The resin was prepared by rinsing 2 times with 10 volumes dry methanol, then dried for several hours under high vacuum for several hours at 40°C.

25      The polymerization results are shown below:

TABLE 7

|    | <u>Sample</u>  | <u>Mn</u> | <u>Mw</u> | <u>PDI</u> | <u>% Conversion</u> |
|----|----------------|-----------|-----------|------------|---------------------|
| 30 | Tin (II) Oxide | 77,228    | 103,161   | 1.34       | 54.0                |
|    | Amberlyst      | 1,112     | 1,498     | 1.34       | 73.5                |

composition.

The viscosity data show significant correlations with molecular weight. This dependence documents the practical limitation and necessity of controlling polymer molecular weight below an upper limit at which it is impractical to melt-process the polymer. At high molecular weight, high viscosity prevents processing by standard melt-processing equipment. Increases in temperature to reduce viscosity dramatically increase polymer degradation and lactide formation which is also unacceptable.

TABLE 8

|             |                            |  | <u>Viscosity at 173°C (Pa·S)</u> |                                |                                 |                       |
|-------------|----------------------------|--|----------------------------------|--------------------------------|---------------------------------|-----------------------|
| Sample I.D. | Meso Lactide In Blend, Wt% | Molecular Weight After Injection Weight                                      | Final IV (dl/g)                  | Shear Rate 100 S <sup>-1</sup> | Shear Rate 1000 S <sup>-1</sup> |                       |
| 6           | 40                         | 41000  | 0.86                             | 5.5                            | 2.9                             |                       |
| 5           | 10                         | 54000  | 0.88                             | 10.4                           | 7.2                             |                       |
| 4           | 20                         | 59000  | 0.91                             | 10.4                           | 7.2                             |                       |
| 8           | 10                         | 64000  | 1.02                             | 15.7                           | 10.0                            |                       |
| 9           | 40                         | 68000  | 0.97                             | 12.6                           | 8.1                             |                       |
| 7           | 20                         | Dataproducts LZR-1230 *MEG* /BGCDA LZR124.PRSies of Injection Molded Samples |                                  |                                |                                 |                       |
| Sample I.D. | Modulus MPa                | Tensile Strength (Yld) PSI   | % Elongation at Break            | IZOD Impact ft. lb./in         | Flexural Modulus MPa            | Flexural Strength PSI |
| 6           | 0.55                       | 6600   | 3.3                              | 0.39                           | 0.53                            | 11300                 |
| 5           | 0.56                       | 7800   | 3.5                              | 0.46                           | 0.54                            | 12500                 |
| 4           | 0.56                       | 7600   | 3.9                              | 0.32                           | 0.53                            | 12500                 |
| 8           | 0.55                       | 7700   | 3.4                              | 0.47                           | 0.53                            | 12400                 |
| 9           | 0.59                       | 6700   | 3.1                              | 0.42                           | 0.52                            | 10600                 |
| 7           | 0.56                       | 7400   | 3.3                              | 0.45                           | 0.51                            | 12400                 |
| 10          | 0.55                       | 6700   | 3.0                              | 0.47                           | 0.52                            | 9900                  |

#### Example 10

##### Effect of Residual Catalyst on Polymer Degradation

Polymer samples were prepared at four levels of catalyst, corresponding to monomer to catalyst molar ratios of 5,000:1, 10,000:1, 20,000:1, and 40,000:1. The catalyst utilized was tin (II) bis(2-ethyl hexanoate). These samples were then subjected to heating in a TGA apparatus (TA Instruments, Inc., model 951 thermogravimetric analyzer with a DuPont 9900 computer support system) with a nitrogen purge. Isothermal conditions of 200°C for 20 minutes were used. The samples were then analyzed by GPC with a viscosity-based detector and a universal calibration curve to determine the extent of breakdown in molecular weight.

catalyst molar ratio, Fascat<sup>®</sup> 2003) was charged through a port in the top of the reactor. The reaction was allowed to proceed for 70 minutes at 180°C, with mechanical agitation. Conversion at this point was 93-94%, close to the equilibrium value at 180°C of 96% poly(lactide) from Figure 2. This point is considered t-zero, designating the completion of the polymerization reaction and the beginning of the mixing time.

In the control experiment, a sample was taken and the mixture was held at temperature with continued agitation. Samples were taken periodically through a port in the reactor bottom. After 4 hours the reactor was drained.

In the example experiment, a sample was taken and 0.25 weight % of a metal deactivator (Irganox<sup>®</sup> MD 1024<sup>®</sup>) was added through the catalyst addition port. The mixture was held at temperature with continued agitation and samples were withdrawn periodically. The reactor was drained after 4 hours.



TABLE 10

|    | Control | Mn     | Mw      | % Polymer | % Oligomer | % Monomer |
|----|---------|--------|---------|-----------|------------|-----------|
| 5  | t-zero  | 67,100 | 119,500 | 94        | 0          | 6.0       |
|    | 0.5 hr  | 62,500 | 119,000 | 95        | 0.7        | 3.9       |
|    | 1.0 hr  | 61,500 | 116,100 | 96        | 0          | 3.6       |
|    | 1.5 hr  | 56,000 | 111,600 | 95        | 1.5        | 3.3       |
|    | 2.0 hr  | 57,600 | 110,900 | 96        | 0.9        | 3.1       |
| 10 | 4.0 hr  | 51,400 | 105,400 | 94        | 3.3        | 3.1       |

|    | Test   | Mn     | Mw      | % Polymer | % Oligomer | % Monomer |
|----|--------|--------|---------|-----------|------------|-----------|
| 15 | t-zero | 63,200 | 110,700 | 93        | 3.5        | 3.8       |
|    | 0.5 hr | 52,100 | 108,600 | 92        | 4.6        | 2.9       |
|    | 1.0 hr | 52,700 | 109,200 | 92        | 4.9        | 2.8       |
|    | 1.5 hr | 53,400 | 107,200 | 93        | 4.0        | 3.1       |
|    | 2.0 hr | 59,700 | 111,100 | 94        | 0.6        | 5.8       |
| 20 | 4.0 hr | 51,200 | 107,300 | 91        | 6.1        | 3.3       |

The samples were then ground and placed in a 120°C oven under vacuum (pressure 0.1 inch Hg) for 14 hours.

25 Sample analyses after this treatment are shown below in Table 11.

TABLE 11

|    | Control | Mn     | Mw      | % Polymer | % Oligomer | % Monomer |
|----|---------|--------|---------|-----------|------------|-----------|
| 30 | t-zero  | 45,500 | 88,500  | 98        | 2.2        | 0.0       |
|    | 0.5 hr  | 45,000 | 88,700  | 98        | 2.0        | 0.0       |
|    | 1.0 hr  | 43,900 | 87,200  | 98        | 2.0        | 0.0       |
|    | 1.5 hr  | 42,600 | 84,000  | 98        | 2.2        | 0.0       |
|    | 2.0 hr  | 42,000 | 85,200  | 97        | 3.2        | 0.0       |
| 35 | 4.0 hr  | 41,900 | 82,800  | 98        | 2.0        | 0.0       |
|    | Test    | Mn     | Mw      | % Polymer | % Oligomer | % Monomer |
| 40 | t-zero  | 39,300 | 76,700  | 96        | 4.0        | 0.0       |
|    | 0.5 hr  | 43,900 | 85,100  | 98        | 2.4        | 0.0       |
|    | 1.0 hr  | 55,300 | 98,600  | 96        | 3.8        | 0.0       |
|    | 1.5 hr  | 48,400 | 96,200  | 95        | 4.5        | 0.0       |
|    | 2.0 hr  | 48,900 | 101,900 | 95        | 5.0        | 0.0       |
| 45 | 4.0     | 50,600 | 101,900 | 94        | 5.6        | 0.0       |

and held for one hour as a simulation of melt-processing. Analysis of the samples after the heat treatment is given below in Table 13.

TABLE 13

| Control | Mn     | Mw     | % Polymer | % Oligomer | % Monomer |
|---------|--------|--------|-----------|------------|-----------|
| t-zero  | 23,900 | 60,000 | 88        | 8.4        | 4.0       |
| 0.5 hr  | 23,900 | 59,600 | 90        | 7.7        | 2.7       |
| 1.0 hr  | 23,700 | 58,800 | 88        | 9.3        | 2.7       |
| 1.5 hr  | 24,700 | 58,000 | 86        | 10.0       | 3.8       |
| 2.0 hr  | 26,100 | 56,400 | 90        | 6.8        | 2.7       |
| 4.0 hr  | 24,800 | 58,700 | 92        | 6.6        | 1.9       |

| Test   | Mn      | Mw     | % Polymer | % Oligomer | % Monomer |
|--------|---------|--------|-----------|------------|-----------|
| t-zero | 33,900  | 64,300 | 95        | 2.2        | 3.1       |
| 0.5 hr | 17,900  | 34,600 | 94        | 4.8        | 1.7       |
| 1.0 hr | 21,200  | 42,900 | 94        | 4.6        | 1.8       |
| 1.5 hr | 29,200  | 56,900 | 98        | 0.5        | 1.8       |
| 2.0 hr | missing |        |           |            |           |
| 4.0 hr | 35,700  | 71,400 | 95        | 3.7        | 1.7       |

The data for molecular weight show that if the metal deactivator is not mixed into the system long enough then it can have a detrimental impact on stability in the melt. The samples Dataproducts LZR-1230 \*M&G\* /HGCDALZR124.PRSight alone. More importantly, the metal deactivator samples show significantly less lactide reformation than the control samples. This effect is gained even in the samples which were mixed for only 0.5 hour. The metals deactivated samples averaged only 1.8% lactide after one hour at 180°C, compared to an average of 3.0% lactide for the controls. The equilibrium level at 180°C is about 3.6% from Figure 2. Thus, the use of metal deactivators can reduce the troublesome reformation of lactide during melt-processing of the finished polymer.

TABLE 14

|    | L/meso    | Temp  | Mn               | Mw                | PDI          | XConv        |
|----|-----------|-------|------------------|-------------------|--------------|--------------|
| 5  | 100% L    | 120°C | 31,014<br>45,864 | 33,774<br>52,574  | 1.09<br>1.15 | 53.2<br>87.1 |
|    | 100% L    | 180°C | 27,785<br>56,839 | 32,432<br>98,125  | 1.17<br>1.73 | 46.7<br>93.3 |
| 10 | 90/10     | 120°C | 34,541<br>29,222 | 38,586<br>34,466  | 1.12<br>1.18 | 62.3<br>89.3 |
|    | 90/10     | 180°C | 31,632<br>57,925 | 35,713<br>110,841 | 1.13<br>1.91 | 48.5<br>94.8 |
| 15 | 70/30     | 120°C | 41,211<br>58,284 | 45,222<br>71,257  | 1.10<br>1.22 | 60.1<br>89.1 |
| 20 | 70/30     | 180°C | 32,292<br>51,245 | 37,401<br>107,698 | 1.16<br>2.10 | 53.8<br>96.5 |
|    | 50/50     | 120°C | 15,888<br>25,539 | 17,969<br>31,834  | 1.13<br>1.25 | 57.8<br>90.6 |
| 25 | 50/50     | 180°C | 34,375<br>44,590 | 42,018<br>98,028  | 1.22<br>2.20 | 62.5<br>95.5 |
| 30 | 100% meso | 120°C | 33,571<br>45,237 | 40,635<br>68,142  | 1.21<br>1.51 | 73.4<br>94.3 |
|    | 100% meso | 180°C | 30,976<br>40,038 | 42,987<br>83,815  | 1.39<br>2.09 | 67.6<br>96.6 |

35

The results show that the ultimate number average molecular weight was not significantly affected by the temperature of polymerization, with an average of 41,000 at 120°C and 50,000 at 180°C. This implies that each lactic acid molecule initiates about one polymer chain, regardless of temperature. The ultimate weight average molecular weight is, however, significantly affected by temperature. At 120°C the weight average molecular weight averaged 52,000 and at 180°C the average was 100,000. This is believed to be due to a relative increase in the rate of transesterification at 180°C. The polydispersity index (PDI) at high conversion also reflects this, averaging 1.3

Test 2

Conditions: vial polymerization, 5000:1 molar ratio of lactide to tin, tin(II) bis(2-ethyl hexanoate) catalyst, 0.25 wt % Ultrinox®626 (in THF). 180°C. Time was 60 minutes. Lactide was used from the above described Gruber et al. process.

The control with tin alone polymerized to 67% conversion and reached a MWn of 62,900. The example with tin and Ultrinox® polymerized to 66% conversion and reached a MWn of 75800; an increase of 21% over the control.

A second example with tin(II) bis(2-ethyl hexanoate), Ultrinox®, and 0.50% of Irganox® 1076, which is a phenolic antioxidant, polymerized to 66% conversion and reached a number average molecular weight (MWn) of 74500; an increase of 18% over the control.

All samples were a dark yellow color, although the samples with stabilizer had a slightly lower absorbance at 300 nm.

Test 3

Conditions: vial polymerization, 10,000:1 molar ratio of lactide to tin, tin(II) bis(2-ethyl hexanoate) catalyst, 180°C, 80% L-lactide and 20% D,L-lactide purchased from Henley and Aldrich, respectively. Lactic acid was added to control molecular weight to about 75,000 at full conversion. One sample included 0.25% Ultrinox® 626 phosphite stabilizer, one included 0.25% Irganox® 1076 antioxidant, and one control sample.

Samples were taken at various times and analyzed by GPC for conversion and molecular weight (the method of Example 7). The results are summarized in Table 15 below.

number average molecular weight to an estimated 80,000 at full conversion. One sample was run with 0.25% Ultrinox® 626 phosphite stabilizer, one with 0.25% Irganox® 1076 antioxidant, and one control sample.

- 5        Samples taken at various times and analyzed by GPC (the method of Example 1) for conversion and molecular weight. The results are tabulated in Table 17 below.

TABLE 17

| Time<br>(hrs) | Control |       | Irganox® |       | Ultrinox® |       |
|---------------|---------|-------|----------|-------|-----------|-------|
|               | Mn      | %conv | Mn       | %conv | Mn        | %conv |
| 1             | 83,600  | 76    | 121,900  | 83    | 162,300   | 87    |
| 4             | 74,400  | 93    | 104,300  | 95    | 123,900   | 96    |
| 24            | 40,200  | 96    | 52,000   | 96    | 96,900    | 97    |
| 48            | 34,200  | 97    | 30,400   | 96    | 56,500    | 96    |
| 72            | 25,000  | 96    | 22,400   | 96    | 69,500    | 96    |

- 20        The phosphite-stabilized sample had a molecular weight more than 60% higher than the control for all time periods. After 72 hours it had a molecular weight 2.8 times higher than the control. The sample with antioxidant showed an initial increase in molecular weight, relative to the control, but the effect disappeared after 48 hours.

25        The phosphite stabilized sample was significantly lighter in color than the control or the antioxidant treated sample.

### 30        Test 6

- Conditions: vial polymerization, 5000:1 molar ratio of lactide to tin, tin(II) bis(2-ethyl hexanoate) catalyst, 0.25 wt % Ultrinox®626 (in THF). 180°C. Time was two hours. Gruber et al. process lactide washed with isopropyl alcohol was used.

35        The control with tin alone polymerized to 95% conversion and reached a number average molecular weight of 118,000. The example with tin and Ultrinox® polymerized to 93% conversion and reached a number average molecular

57

TABLE 18

|    | <u>Sample</u> | <u>MWn</u> | <u>% Conversion</u> | <u>Relative Rate</u> |
|----|---------------|------------|---------------------|----------------------|
| 5  | Control 1     | 65,000     | 95.9                | 90                   |
|    | Control 2     | 85,000     | 95.9                | 100                  |
|    | Control 3     | 76,000     | 96.6                | 100                  |
|    | Control 4     | 69,000     | 96.2                | 100                  |
|    | Control 5     | 74,000     | 96.8                | 110                  |
| 10 | Control 6     | 70,000     | 97.2                | 110                  |

PHOSPHITES

|    |                 |              |         |      |     |
|----|-----------------|--------------|---------|------|-----|
| 15 | Ultrinox 626    | (GE)         | 103,000 | 96.8 | 100 |
|    | Weston TDP      | (GE)         | 64,000  | 70.0 | 60  |
|    | Weston PDDP     | (GE)         | 67,000  | 76.7 | 60  |
|    | Weston PNPG     | (GE)         | 92,000  | 94.1 | 100 |
|    | Irgafos 168     | (Ciba-Geigy) | 95,000  | 95.3 | 120 |
| 20 | Weston 618      | (GE)         | 99,000  | 95.1 | 100 |
|    | Sandostab P-EPQ | (Sandoz)     | 108,000 | 94.7 | 110 |
|    | Weston TNPP     | (GE)         | 88,000  | 97.9 | 130 |

25 PHENOLIC ANTIOXIDANTS

|    |              |              |         |      |     |
|----|--------------|--------------|---------|------|-----|
|    | Irganox 1010 | (Ciba-Geigy) | 95,000  | 97.5 | 110 |
|    | Cyanox 1790  | (Cyanamid)   | 98,000  | 96.9 | 120 |
|    | BHT          |              | 87,000  | 96.5 | 130 |
| 30 | Irganox 1076 | (Ciba-Geigy) | 121,000 | 97.8 | 130 |
|    | Topanol CA   | (ICI)        | 84,000  | 96.6 | 160 |

AMINES

|    |             |              |        |      |     |
|----|-------------|--------------|--------|------|-----|
| 35 | Tinuvin 123 | (Ciba-Geigy) | 65,000 | 94.8 | 70  |
|    | Tinuvin 622 | (Ciba-Geigy) | 82,000 | 95.7 | 80  |
|    | Naugard 445 | (Uniroyal)   | 93,000 | 98.2 | 120 |

40

THIOETHER

|  |           |         |        |      |     |
|--|-----------|---------|--------|------|-----|
|  | Mark 2140 | (Witco) | 77,000 | 97.0 | 120 |
|--|-----------|---------|--------|------|-----|

45

METAL DEACTIVATORS

|  |                |              |        |      |     |
|--|----------------|--------------|--------|------|-----|
|  | Irganox MD1024 | (Ciba-Geigy) | 34,000 | 65.7 | 10  |
|  | Naugard XL-1   | (Uniroyal)   | 91,000 | 95.8 | 110 |

TABLE 19

| 5  | <u>Sample</u>                               | <u>Extruder<br/>Temperature (C)</u> | <u>Weight Average<br/>Molecular Weight</u> |
|----|---|-------------------------------------|--|
|    | Initial                                     |                                     | 63,000                                     |
| 10 | Dried 1 hour<br>(1200 ppm H <sub>2</sub> O) | 137<br>145<br>162<br>179            | 44,000<br>48,000<br>35,000<br>30,000       |
| 15 | Dried 4 hours<br>(150 ppm H <sub>2</sub> O) | 140<br>140<br>160<br>178            | 63,000<br>69,000<br>65,000<br>68,000       |
| 20 |   |                                     |  |

These results show the detrimental effect of water in the lactide polymer resin during melt polymerization and the need to properly dry the poly(lactide) before melt-processing.

25

Example 15Degradation of Crystalline and  
Amorphous Poly(lactide)

30 Two literature references disclose poly(D,L- lactide) to degrade faster than poly(L-lactide), attributing the result to crystallinity of poly(L-lactide). These are: Kulkarni et al., J. Biomed. Mater. Res., vol. 5, pp. 169-181, (1971); Makino et al., Chem. Pharm. Bull., vol. 33, 35 pp. 1195-1201, (1985). An experiment was conducted to measure the effect of crystallinity on polymer degradation and is detailed below.

An amorphous poly(lactide) sample (clear, and less than 1% crystallinity based on DSC) and a crystalline 40 poly(lactide) sample (opaque, and approximately 50% crystallinity based on DSC) were subjected to biodegradation in a compost test (50°C, with aeration). The DSC apparatus was a TA Instruments, Inc., model 910

Example 16Effect of Monomer Concentration on Film Modulus

Poly(lactide) was precipitated in methanol from a chloroform solution in order to remove the residual lactide monomer. GPC analysis (the method of Example 1) showed the precipitated polymer to contain 0.0% lactide.

The polymer was dissolved in chloroform to make a 10 wt% solution, and lactide was added back to make 5 separate solutions which, after removing the chloroform, are calculated to produce films containing 0.0, 0.2, 0.4, 1.0 and 4.0 weight% lactide in poly(lactide). These solutions were solvent cast onto glass, dried overnight at room temperature in a fume hood, and removed to a vacuum oven. The films were hung in the vacuum oven and dried at 30°C for 72 hours. GPC analysis of the vacuum-dried films showed measured lactide levels of 0.0, 0.0, 0.4, 0.7 and 3.7 wt%.

The films were then tested for film modulus using ASTM procedure D882.

The results are shown below in Table 20.

TABLE 20

|    | Z<br>Lactide | Tensile<br>(psi avg.) | Std.<br>Dev. | Z<br>Elongation | Std.<br>Dev. | Elastic<br>Modulus<br>(psi avg.) | Std.<br>Dev. |
|----|--------------|-----------------------|--------------|-----------------|--------------|----------------------------------|--------------|
| 25 | 0            | 5490                  | 636          | 2.85            | 0.14         | 730,000                          | 103,000      |
|    | 0            | 6070                  | 123          | 2.85            | 0.22         | 818,000                          | 35,000       |
| 30 | 0.4          | 5670                  | 227          | 2.75            | 0.27         | 779,000                          | 44,000       |
|    | 0.7          | 5690                  | 343          | 4.04            | 1.12         | 749,000                          | 58,000       |
|    | 3.7          | 5570                  | 458          | 3.33            | 1.43         | 738,000                          | 66,000       |



portions of the vial is included in the product work-up and test.

Melt-stabilized poly(lactide) will show less than 2% lactide in the 15 minute sample, and more preferably less than 2% lactide in the 1 hour sample. The most highly stabilized poly(lactide)s will maintain lactide contents of less than 1% in both the 15 minute and 1 hour samples, preferably less than 0.5%. An unstabilized poly(lactide) may reach the equilibrium lactide content at 180°C of 3.6 wt%, or may go even higher as lactide is driven from the polymer melt and collects on the cooler top walls of the vial.

#### Example 19

##### Water Scavenger Experiments

Dried poly(lactide) pellets were processed in a twin screw extruder to devolatilize and to prepare a portion with 0.5% by weight of a water scavenger (Stabaxol® P). The strands leaving the extruder are cooled in a water trough and chopped into pellets. Samples of the control and the test sample were then analyzed by the Karl Fischer technique for moisture content, with no drying. The control sample contained 1700 ppm water, the test sample had 450 ppm water. The control sample was then dried under nitrogen at 40°C, reducing the water content to 306 ppm. A vacuum-dried control sample had 700 ppm water.

The as-produced test sample and the dried control samples were then processed in a 1/2" single screw extruder (Brabender®) at 160°C, with a retention time of 3 minutes. The number average molecular weight for the dried control sample dropped from an initial value of 44,000 to a final value of 33,000 for the 306 ppm water sample and to 28,000 for the 700 ppm water sample. The test sample number average molecular weight dropped from an initial value of 40,000 to a final value of 33,000.

TABLE 22

|    | Sample  | Time<br>(min) | Number Average<br>Molecular Weight | Weight Average<br>Molecular Weight | Lactide<br>Weight % |
|----|---------|---------------|------------------------------------|------------------------------------|---------------------|
| 5  | 1000:1  | 0             | 39,000                             | 81,300                             | 0.8                 |
|    |         | 5             | 28,100                             | 57,300                             | 2.4                 |
|    |         | 15            | 25,800                             | 49,700                             | 2.8                 |
|    |         | 30            | 23,100                             | 43,800                             | 3.7                 |
| 10 |         | 60            | 22,800                             | 43,200                             | 3.6                 |
|    | 3000:1  | 0             | 53,100                             | 113,600                            | 0.6                 |
|    |         | 5             | 39,000                             | 76,400                             | 0.4                 |
|    |         | 15            | 30,300                             | 65,400                             | 1.9                 |
| 15 |         | 30            | 29,000                             | 60,400                             | 2.7                 |
|    |         | 60            | 28,200                             | 55,200                             | 2.8                 |
|    | 20000:1 | 0             | 89,200                             | 184,000                            | 0.0                 |
|    |         | 5             | 81,200                             | 165,100                            | 0.0                 |
| 20 |         | 15            | 54,300                             | 134,600                            | 0.1                 |
|    |         | 30            | 51,100                             | 119,600                            | 0.0                 |
|    |         | 60            | 49,500                             | 111,000                            | 0.0                 |

These results show the benefit of optimizing the catalyst level used in the polymerization process. Note that both lactide reformation and molecular weight retention benefits are realized from the reduced catalyst levels (higher monomer/catalyst ratio).

It is believed catalyst levels should be limited to 1000:1 for the high end of catalyst usage, with 3000:1 being more preferable and showing somewhat improved stability. Lower levels still, such as 20000:1, show greatly improved stability. Beyond this level it is believed the polymerization rates become too slow to be practical.

The measured tin level in the precipitated polymer was 337 ppm by weight, compared to a calculated value of 466 ppm for the as-produced polymer. This result indicates the feasibility of reducing residual catalyst levels in lactide polymers by solvent precipitation with the benefit of improved stability as detailed in Example 20.

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Example 22

Samples of devolatilized poly(lactide) were tested in a Rosand Model 14°C capillary rheometer. The die was 1 mm diameter and 16 mm long, with an entry angle of 180°. The table below gives the pressure drop across the die as a function of nominal shear rate (not Rabinowitsch corrected) for various molecular weights and temperatures.

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Results at 175°C.

|    | <u>Mn</u> | <u>MW</u> | <u>Temp. (°C)</u> | <u>Nominal<br/>shear rate<br/>(s<sup>-1</sup>)</u> | <u>Pressure<br/>Drop<br/>(MPa)</u> |
|----|-----------|-----------|-------------------|--|------------------------------------|
| 5  | 34,000    | 70,000    | 175               | 192  | 0.4                                |
|    |           |           |                   | 384  | 0.5                                |
|    |           |           |                   | 960  | 3.4                                |
| 10 |           |           |                   | 1920   | 5.5                                |
|    |           |           |                   | 4800   | 9.2                                |
|    |           |           |                   | 9600   | 12.5                               |
| 15 | 52,000    | 108,000   | 175               | 192  | 2.2                                |
|    |           |           |                   | 384  | 4.6                                |
|    |           |           |                   | 960  | 7.6                                |
|    |           |           |                   | 1920   | 11.5                               |
|    |           |           |                   | 4800   | 17.2                               |
|    |           |           |                   | 9600   | 22.1                               |
| 20 | 183,000   | 475,000   | 175               | 192  | 11.5                               |
|    |           |           |                   | 384  | 16.6                               |
|    |           |           |                   | 960  | 20.2                               |
| 25 |           |           |                   | 1920   | 24.4                               |
|    |           |           |                   | 4800   | 29.9                               |
|    |           |           |                   | 9600   | ----                               |

30 Results at 200°C.

|    | <u>Mn</u> | <u>MW</u> | <u>Temp. (°C)</u> | <u>Nominal<br/>shear rate<br/>(s<sup>-1</sup>)</u> | <u>Pressure<br/>Drop<br/>(MPa)</u> |
|----|-----------|-----------|-------------------|--|------------------------------------|
| 35 | 60,000    | 137,000   | 200               | 192  | 0.5                                |
|    |           |           |                   | 384  | 1.6                                |
|    |           |           |                   | 960  | 3.3                                |
|    |           |           |                   | 1920   | 5.3                                |
| 40 |           |           |                   | 4800   | ----                               |
|    |           |           |                   | 9600   | 13.2                               |
| 45 | 183,000   | 475,000   | 200               | 192  | 7.0                                |
|    |           |           |                   | 384  | 11.0                               |
|    |           |           |                   | 960  | 14.2                               |
|    |           |           |                   | 1920   | 17.9                               |
|    |           |           |                   | 4800   | 21.6                               |
|    |           |           |                   | 9600   | ----                               |

Table 24

| <u>First upheat</u>  |                          | <u>Exotherm<br/>(J/gm)</u> | <u>Peak Temp.<br/>(°C)</u> | <u>Endotherm<br/>(J/gm)</u> | <u>Peak Temp.<br/>(°C)</u> |
|----------------------|--------------------------|----------------------------|----------------------------|-----------------------------|----------------------------|
|                      | <u>Sample &amp; meso</u> |                            |                            |                             |                            |
| 5                    | 0                        | 29.1                       | 114                        | 33.7                        | 172                        |
|                      | 3                        | 4.4                        | 126                        | 5.9                         | 159                        |
|                      | 6                        | 0                          | ---                        | 0                           | ---                        |
| 10                   | 9                        | 0                          | ---                        | 0                           | ---                        |
| <u>Second upheat</u> |                          |                            |                            |                             |                            |
| 15                   | 0                        | 14.1                       | 137                        | 12.2                        | 173                        |
|                      | 3                        | 0                          | ---                        | 0                           | ---                        |
|                      | 6                        | 0                          | ---                        | 0                           | ---                        |
|                      | 9                        | 0                          | ---                        | 0                           | ---                        |
| 20                   |                          |                            |                            |                             |                            |

Figure 3 shows the sharp decline in potential crystallinity between 9 and 12% meso content.

In contrast, a polymer sample made by polymerizing 80% L-lactide and 20% D,L-lactide showed, after annealing, a melting endotherm of 12.3 J/gm. This composition has the same enantiomeric excess in terms of lactide acid R- and S-units as does an 80% L-lactide/20% meso-lactide blend. The 20% meso-lactide containing blend showed no crystallinity after annealing, as shown by Figure 3.

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#### Example 25

##### Effect of Plasticizer on Crystallization Rate

Devolatilized polymer samples from a continuous pilot plant were compounded with dioctyl adipate (a plasticizing agent) and/or silica with a twin screw extruder. The samples were then tested for nucleation rates using the DSC method of Example 23. The table below shows that dioctyl adipate (DOA) can increase the rate of crystallization of poly(lactide) or of a filled poly(lactide).

Example 26An Evaluation of Nucleating Agents

A devolatilized sample of poly(lactide) polymer was compounded with a variety of potential nucleating agents in a single screw extruder. The candidate nucleating agents were added at a nominal level of 5% by weight. The single screw extruder is not as effective of a mixer as would be used commercially, so failure to observe an effect in these tests does not mean that a candidate agent would not be effective if blended more thoroughly. A positive result in this test demonstrates potential ability to increase crystallization rates. Additives which increased crystallinity in the second upheal (on a quenched sample) were rated ++, additives which showed an effect only on the first upheal were rated +, and additives which showed no effect were rated 0.

reduced the crystallization rate, although the effect of orientation did not disappear. It is believed that a longer hold time in the melt would eliminate the effect of orientation.



It will be understood that even though these numerous characteristics and advantages of the invention have been set forth in the foregoing description, together with details of the structure and function of the invention, the disclosure is illustrative only, and changes may be made in detail, especially in matters of shape, size and arrangement of the parts or in the sequence or the timing of the steps, within the broad principle of the present invention to the full extent indicated by the broad general meaning of the terms in which the appended claims are expressed.

4. A fabric according to claim 1 wherein:

(a) said poly(lactide) fibers further comprise fibers formed from a melt stable lactide polymer composition comprising poly(lactide) chains having a number average molecular weight from about 50,000 to about 250,000.

5. A fabric according to claim 1 wherein:

(a) said poly(lactide) fibers are arranged as a nonwoven fabric;

(b) said poly(lactide) polymer chains have a number average molecular weight of from about 10,000 to about 300,000; and,

(c) said fibers are formed from a melt stable lactide polymer composition including no more than about 2000 parts per million water.

6. The nonwoven fabric of claim 5 wherein said plurality of poly(lactide) polymer chains have a number average molecular weight from about 50,000 to about 250,000.

7. The nonwoven fabric of claim 5 wherein said plurality of poly(lactide) polymer chains have a number average molecular weight from about 20,000 to about 80,000.

8. The nonwoven fabric of claim 5 wherein said polymer chains are reaction products of polymerizing a lactide mixture comprising about 9 to about 50 percent by weight meso-lactide and the remaining lactide is substantially L-lactide and D-lactide.

14. The nonwoven fabric of claim 5, wherein said fibers are formed from a melt stable lactide polymer composition including a desiccant selected from the group consisting of: clay, alumina, silica gel, zeolites, calcium chloride, calcium carbonates, sodium sulfate, bicarbonates and mixtures thereof.

15. The nonwoven fabric of claim 5 wherein said polymer composition further comprises:

- (a) catalyst means for catalyzing the polymerization of lactide to form the poly(lactide) polymer chains, said catalyst means incorporated into the melt-stable lactide polymer composition during polymerization; and
- (b) a catalyst deactivating agent in an amount sufficient to reduce catalytic depolymerization of said poly(lactide) polymer chains.

16. A compostable bag comprising the nonwoven fabric of claim 5.

17. The fabric of claim 1 wherein said poly(lactide) fibers include melt blown fibers.

18. The fabric of claim 16 wherein said melt blown fibers have a diameter of less than about 5  $\mu\text{m}$ .

19. The fabric of claim 1 wherein said poly(lactide) fibers include fibers from a spunbond process.

20. The fabric of claim 1 wherein said polymer composition further includes a plasticizer.

- 5 (i) poly(lactide) polymer chains,  
said polymer chains being reaction  
products of polymerizing a lactide mixture  
comprising a lactide component including  
about 0.5 to about 50 percent, by weight,  
meso-lactide, with the remaining lactide  
component being selected from the group  
10 consisting of L-lactide, D-lactide and  
mixtures thereof, said polymer chains  
having a number average molecular weight  
of at least about 10,000;
- 15 (ii) lactide in a concentration of  
less than about 2 percent by weight; and  
(iii) water in a concentration of  
less than about 2000 parts per million;
- (b) extruding said polymer composition  
into fibers; and,
- 20 (c) forming the fibers into the fabric.

25 25. The process of claim 24 wherein said step  
of extruding is a melt blown process; and the  
lactide polymer composition comprises poly(lactide)  
polymer chains having a number average molecular  
weight of about 20,000 to about 80,000.

30 26. The process of claim 24 wherein said step  
of extruding is a spunbond process; and, the lactide  
polymer composition comprises poly(lactide) polymer  
chains having a number average molecular weight from  
about 75,000 to about 200,000.

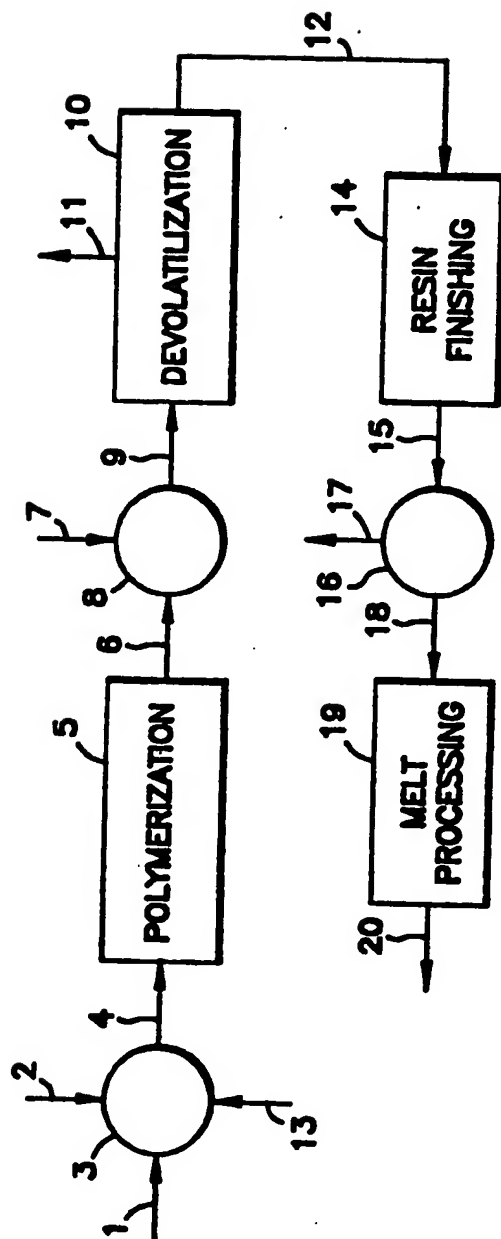
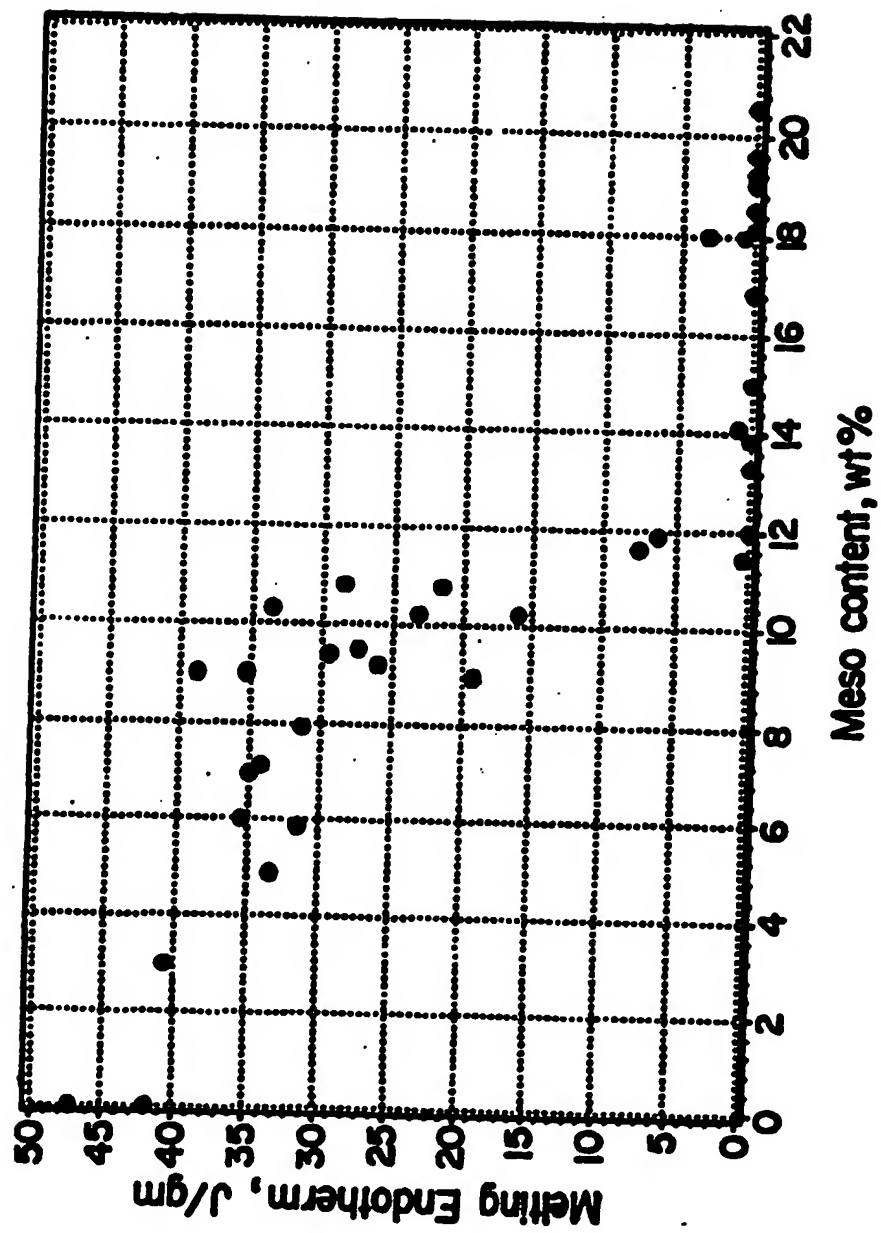


FIG. 1

FIG. 3



SUBSTITUTE SHEET

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int ional Application No

PCT/US 93/09308

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